

[0011] As for the content of photocatalyst semiconductor particles, it is desirable that it is 5 to 70% of full weight of plastic solid. It is because that coat formation will become difficult if the content of photocatalyst semiconductor particles is too large. It is because that when the content of photocatalyst semiconductor particles is too small, the characteristics of photocatalyst is hard to be obtained.

[0013] As photocatalyst grains, especially titanium oxide has high photocatalyst ability, is chemically stable. Since titanium oxide is harmless, it is desirable as photocatalyst particle. Any one of Anatase type, Rutile type, and Brookite type or these mixtures may be sufficient as the crystal system of titanium oxide. The titanium oxide in which surface is modified can also be used preferably. The titanium oxide includes the titanium oxide in which surface in part at least with silica, alumina, silica alumina, a zinc oxide, an apatite, PTFE resin, etc. For example, the photocatalyst covered with porous inorganic substances, such as silica, can be used preferably. As for the hole diameter of the enveloping layer which consists of a porous inorganic substance, the hole diameter of about 5 Angstrom to 1000 Angstrom is desirable, and more preferably, the hole diameter of about 100 Angstrom to 300 Angstrom is desirable.

If an aperture of the porous inorganic substance is large, titanium oxide will be contacted direct to a substrate and special binder protection nature will be lost. If an aperture of the porous inorganic substance is too small, a pollutant will not reached to a photocatalyst.

As explained, the titanium oxide in which surface is modified could suppress the decomposition of the supporting layer and had the outstanding point that supporting layer having broad width could be used. In the former art, catalytic activity, such as a self-consecration operation by a photocatalyst, could be decreased to some extent.

As the surface of photocatalyst semiconductor particles is exposed like the present invention and the sufficient catalytic activity is acquired even by using the titanium oxide in which surface is modified, such titanium oxide can be especially used preferably.

Further, since the titanium oxide has the ultraviolet absorption ability, the

difference was produced also in degradation by the sunlight exposure to supporting layer itself when the surface of titanium oxide is exposed or not with the same titanium oxide addition. The titanium in which surface is exposed also has the special feature that cannot be turned to yellow easily.

[0021] The plastic solid according to the present invention may be made by coating onto the textile structure such as woven consisting of polyester or nylon fiber. These plastic solid may be made by coating the plastic sheet covered by resin to at least one side of textile structure or by attaching the plastic sheet formed like a film to at least one side of textile structure.

The textile structure having a sheet shape can be used as a general structural material, especially, for example, the hood of transporter apparatus such as a truck sheet, a roof of a tentorium warehouse, an open freighting sheet, the decoration sheet for stores, eaves broth tentorium, the roof of various arcades, the cover of the side of pavilion of a show, etc., a waterproof protection sheet, a protection-against-snow sheet, an air dome, a pool cover, etc. can be used widely. Since a surface beautiful state is held over a long period of time, it can be used preferably.

[0022] In many cases in the textile structure used for above mentioned application, textile structure are sewed with the thermal welding by using such as a high frequency welder and Leister. It is desirable for the supporting layer containing a photocatalyst to be thermoplastic synthetic resin.

[0023] This invention is explained using a drawing. FIG. 1 illustrates a cross section of the plastic solid in which the photocatalyst semiconductor particles of 1 contain in the supporting layer of 2. FIG. 1 shows that photocatalyst semiconductor particles are further exposed with a physical or a chemical method.

[0024] FIG. 2 shows the graph of the weight loss under the UV of 10 mw/cm<sup>2</sup> irradiated to Examples of the present invention on which surfaces are coated with salad oil of 0.1mg/cm<sup>2</sup>. Numerals A, B, C, D, E, and F in the figure show the weight loss of Examples 1, 2, 3, 4, 5, and 6, respectively.

[0025] FIG. 3 shows the graph of the weight loss under the UV of 10 mw/cm<sup>2</sup> irradiated to Comparative Examples of the present invention on

which surfaces are coated with salad oil of  $0.1\text{mg}/\text{cm}^2$ . Numerals G, H, I and J of the FIG. 3 show the weight loss of the comparative examples 1, 2, 3 and 4, respectively.

[0026]

[Example] Hereinafter, the present invention will be explained still more in detail by examples.

[0027] The values in performance as shown in Examples and Comparative Examples were measured by the following method.

<Organic substance resolution power>

The photocatalyst semiconductor particle contained layer was cut into  $2.5\text{ cm} \times 5\text{ cm}$ , and it was pasted up with the double-sided tape so that a photocatalyst containing layer might come out on the surface on slide glass  $2.6\text{cm}\times 7\text{ cm}$ . On the surface of the photocatalyst containing layer, the salad oil (made by the Nisshin Oil Mills, Ltd.) was coated so that it might become  $0.1\text{ mg}/\text{cm}^2$ . It is put into the ultraviolet light illumination apparatus (made by a great Japan plastic company) adjusted so that UV irradiation intensity might become  $10\text{ mw}/\text{cm}^2$ .

The minute reductions of the weight of salad oil in every one (1) hour were measured for 5 hours, and the reduction weight of salad oil per hour per  $1\text{ cm}^2$  were measured. These datum were plotted to pass along the starting point as initial inclination, the inclination of the primary approximate expression by 2 hours was calculated as the organic substance resolution power, and it is expressed as  $\mu\text{ g}/\text{cm}^2/\text{hour}$ .

It is shown that organic substance resolution power is so high that the absolute value of initial inclination is large.

<Antifouling property>

It carried out for 30 days by the method to which outdoor-exposure stain testing is specified JIS A 1410. The brightness (L value) was measured for the surface of the sheet before contamination, and the sheet after exposure by the digital colorimeter color difference computer (made by Suga Test Instruments Co., Ltd.). And the grade of contamination was calculated by the following formula. It can be said that as smaller the value of delta L is, the fall of brightness is small and excellent in antifouling property.

[0028] antifouling property:  $\cdots \delta = A - B$ ,

where A is a L value before stain testing and B is a L value after an outdoor exposure.

#### EXAMPLE 1

The 5 weight % of silicone coating agent (solid content 20% by weight, made by Dow Corning Toray Silicone, Inc., SR2410) and 6.7 weight% of dispersion solution including titanium oxide (content of TiO<sub>2</sub> is 15%, by Sumitomo Osaka Cement Company, PCT-15T) were mixed. These mixtures were coated on one side of 50-micron-thick polyester film by the bar coating machine and dried at 130 degrees centigrade x 5 minutes. Thus, Example 1 was manufactured. The solid content of titanium oxide to the binder resin solid content 1 was 1. The organic substance resolution power was 20 microg/cm<sup>2</sup>/hour.

#### [0029] EXAMPLE 2

About 10 microns of surfaces of Example 1 were ground with abrasive paper (made by Nihon Kenshi Co., Ltd., CC2000-Cw), and Example 2 was manufactured. The organic substance resolution power was 21 microg/cm<sup>2</sup>/hour.

#### EXAMPLE 3

The 10 weight % of polyester resin coating agent (solid content 30% by weight, made by Toyobo Co., Ltd., Byran20SS) and 3 g of titanium oxide fine particles (made by Ishihara Sangyo Kaisha, Ltd., ST-01) were mixed. These mixtures are coated on the polyester film and dried like Example 1, and Example 3 was manufactured. The solid content of titanium oxide to the binder resin solid content 1 was 1. The organic substance resolution power was 20 microg/cm<sup>2</sup>/hour.

#### EXAMPLE 4

The film obtained Example 3 was immersed in sodium hydroxide solution 3% for 24 hours, and the polyester resin surface was hydrolyzed. The film was pulled up, it rinsed and dried, and Example 4 was manufactured. The organic substance resolution power was 22.5 microg/cm<sup>2</sup>/hour.

#### EXAMPLE 5

The polyester resin coating agent 10 weight % of Example 3 and 3 g of

titanium oxide particles in which surface is modified by silica (mean-particle-diameter of 4 microns, specific surface area of 540 microns) were mixed. These mixtures are coated on the polyester film and dried like Example 1. The solid content of titanium oxide to the binder resin solid content 1 was 1. The film was immersed in sodium hydroxide solution 3% like Example 4 for 24 hours, and polyester resin was hydrolyzed. The film was pulled up, it rinsed and dried, and Example 5 was manufactured. The organic substance resolution power was 9 microg/cm<sup>2</sup>/hour.

#### EXAMPLE 6

10 % of weight of urethane resin coating agent (made by Dainippon Ink, Inc., Chris Bon NY331) and 2.5 % of weight of titanium oxide particles in which surface is modified by silica of Example 5 were mixed. These mixtures are coated on the polyester film and dried like Example 1. The solid content of titanium oxide to the binder resin solid content 1 was 1. About 10 microns of the film was ground like Example 2, and Example 6 was manufactured. The organic substance resolution power was 11 microg/cm<sup>2</sup>/hour.

#### COMPARATIVE EXAMPLE 1

10 % of weight of silicone coating agent of Example 1 and 2 % of weight of titanium oxide fine particle of Example 3 were mixed. These mixtures are coated on the polyester film and dried like Example 1, and the Comparative Example 1 was manufactured. The solid content of titanium oxide to the binder resin solid content 1 was 1. Organic substance resolution power was 0.5 microg/cm<sup>2</sup>/hour.

#### COMPARATIVE EXAMPLE 2

The titanium oxide coating film of Example 5 before hydrolysis was made into the Comparative Example 2. The organic substance resolution power was 0.9 microg/cm<sup>2</sup>/hour.

#### COMPARATIVE EXAMPLE 3

The titanium oxide coating film of Example 6 before grinding was made into the Comparative Example 3. The organic substance resolution power was 0.5 microg/cm<sup>2</sup>/hour.

#### COMPARATIVE EXAMPLE 4

The 50-micron polyester film used in the examples was made into the Comparative Example 4. The organic substance resolution power was 0.005 microg/cm<sup>2</sup>/hour. The organic substance resolution power and antifouling property of Examples 1-6 and the comparative examples 1-4 are shown in Table 1.

[0030]

[Table 1]

	Organic substance resolution power ( $\mu\text{g}/\text{cm}^2/\text{hour}$ )	Antifouling property $\Delta L$
EXAMPLE 1	20	1.0
EXAMPLE 2	21	1.7
EXAMPLE 3	20	1.2
EXAMPLE 4	22.5	1.5
EXAMPLE 5	9	2.0
EXAMPLE 6	11	2.0
COMPARATIVE EXAMPLE 1	0.5	6.5
COMPARATIVE EXAMPLE 2	0.9	5.5
COMPARATIVE EXAMPLE 3	0.5	7.0
COMPARATIVE EXAMPLE 4	0.005	7.0

[0031] It can be said that the thing of Examples 1-6 have the antifouling property in which fall delta L of brightness were all small and excellent compared with the thing of the comparative examples 1-4.

[0032]

[Effect of the Invention]

The plastic solid and the textile structure which uses the plastic solid of the present invention are preferably used for all the life materials and industrial materials in which antifouling by a photocatalyst, deodorization,

and an antibacterial effect are expected. They can be used widely as a roof of the tentorium warehouse excellent in especially the antifouling property at the time of an outdoor use, especially, the hood of transporter apparatus such as a truck sheet, the cover of the side of an open freighting sheet, the decoration sheet for stores, eaves broth tentorium, the roof of various arcades, the pavilion of a show, etc., a waterproof protection sheet, a protection-against-snow sheet, an air dome, a pool cover, etc. Since a surface beautiful state is held over a long period of time, it can be used preferably.

## DECLARATION

I, Dr. Kaoru MOTOYA, a national of Japan, 6th floor, Shinjukugyoen Bldg., 3-10, Shinjuku 2-chome, Shinjuku-ku, Tokyo 160-022, JAPAN do hereby solemnly and sincerely declare :

- (1) THAT I am well acquainted with the Japanese language and English language, and
- (2) THAT the attached is a partial, true and faithful translation into the English language checked by me of true copy of Japanese Laid Open Patent Application No. JP 2002- 282703 by the Japanese Patent Office on October 2, 2002.

And, I, Dr. Kaoru MOTOYA, being sworn state that the fact set forth above are true.

Signed this 16th day of March, 2010

Kaoru Motoya  
Dr. Kaoru MOTOYA